

## REE abundance patterns for lanthanite-(Nd) and kimuraite-(Y) regressed successfully by Jørgensen-Kawabe equation for the lanthanide tetrad effect

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### ABSTRACT

The REE abundance patterns for lanthanite-(Nd) [(La, Nd)<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>·8H<sub>2</sub>O] and kimuraite-(Y) [CaY<sub>2</sub>(CO<sub>3</sub>)<sub>4</sub>·6(H<sub>2</sub>O)], have been examined by Jørgensen-Kawabe equation for the lanthanide tetrad effect. The reported REE data for lanthanite-(Nd) samples from the Whitianga quarry, New Zealand (Graham *et al.*, 2007) and Hizen, Higashi Matsuura, Japan (Akagi *et al.*, 1996), give their chondrite-normalized REE patterns which can be regressed successfully by the theoretical equation, except for their Ce anomalies. When the lanthanite-(Nd) from Whitianga is normalized by the Hizen lanthanite, their strong trends of light REE enrichment are cancelled mutually, leaving a small convex tetrad effect in the REE pattern. Two kimuraite-(Y) samples coexisting with the Hizen lanthanite-(Nd) show similar W-type tetrad effects (Akagi *et al.* 1993). One kimuraite-(Y) sample, in fact, exhibits a typical tetrad effect, but the other kimuraite-(Y) shows a less symmetrical one. The REE pattern for the former kimuraite, when normalized by chondrite or by the Hizen lanthanite, is immediately regressed by the theoretical equation, but the REE pattern for the latter kimuraite cannot be fitted to the equation without correcting for light REEs. The excesses of light REEs in the latter kimuraite are evaluated by the regular REE fractionation between kimuraite and lanthanite and the theoretical equation. The REE patterns for lanthanite-(Nd) and kimuraite-(Y) with the tetrad effects are certainly described quantitatively by Jørgensen-Kawabe equation, signifying its importance in considering the REE distributions in the representative rare earth minerals of lanthanite-(Nd) and kimuraite-(Y).

### INTRODUCTION

Nagashima *et al.* (1986) reported a mineralogical and chemical study of rare-earth carbonate hydrate minerals, lanthanite-(Nd) [Nd<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>·8H<sub>2</sub>O], kimuraite-(Y) [CaY<sub>2</sub>(CO<sub>3</sub>)<sub>4</sub>·6(H<sub>2</sub>O)], and lokkaite-(Y) [CaY<sub>4</sub>(CO<sub>3</sub>)<sub>7</sub>·9(H<sub>2</sub>O)], from fissure-filling spherulitic aggregates in the Cenozoic alkali olivine basalt in Hizen-cho, Higashi Matsuura-gun, Saga Prefecture, Kyushu, Japan. Akagi *et al.* (1993) made re-determinations of rare earth elements in Hizen kimuraite samples of Nagashima *et al.* (1986) by ID-MS for

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polyisotopic REE and by ICP-MS for monoisotopic REE (Pr, Tb, Ho, and Tm). They demonstrated that the chondrite-normalized REE patterns for kimuraite samples exhibit similar W-type tetrad effects. Subsequently, Akagi *et al.* (1996) reported the REE data by ID-MS for the lanthanite-(Nd) coexisting with the kimuraite and those for the host basalt samples with and without acid-leaching, together with Nd isotopic ratios of kimuraite and the host basalt leached by HCl solution.

According to Akagi *et al.* (1996), the lanthanite-(Nd) shows a strong enrichment of light REE relative to the kimuraite-(Y), but the trend is reasonably smooth, so that they understood that the lanthanite-(Nd) also involves the W-type tetrad effect similar to that of kimuraite. They noted that the pair of lanthanite and kimuraite possibly formed from a common aqueous solution enriched in REE infiltrated into fissures of the host basalt. They also concluded that the source of aqueous REE solution to have produced the REE carbonate hydrate assemblage may not be the host basalt, because the Nd isotopic ratio of  $\epsilon(\text{Nd}) = -1.13$  for kimuraite is lower than  $\epsilon(\text{Nd}) = +0.84$  for the host basalt leached with 0.5 N HCl solution.

Lanthanite and kimuraite exhibiting the W-type tetrad effect (Akagi *et al.*, 1993 and 1996) are important for REE geochemistry, because they provide the evidence against such a skeptical understanding that reported tetrad effects are mostly attributable to analytical artifacts (McLennan, 1994). In the case of lanthanite and kimuraite, rare earth elements are the major constituents of acid-soluble hydrate minerals, so that analytical difficulty of REE must be insignificant, unlike the REE analyses of igneous rocks supposed by McLennan (1994).

Recently, Graham *et al.* (2007) published the mineralogical and chemical data for the lanthanite-(Nd) in the Whitianga quarry, Coromandel Peninsula, New Zealand. The lanthanite-(Nd) occurs in a tuffaceous, altered andesitic agglomerate in the quarry. They noted that REEs of the lanthanite-(Nd) were possibly scavenged by warm waters circulating through underlying Late Jurassic low-grade metagreywacke sequences. Graham *et al.* (2007) reported the chemical composition of lanthanite-(Nd) concerning all the REE but Tm by ICP-MS, and wrote that the chondrite-normalized REE abundance pattern for lanthanite-(Nd) shows a strong light REE enrichment with a concave downward curve, together with a negative Ce anomaly.

Since the REE data for Hizen lanthanite-(Nd) are those by ID-MS (Akagi *et al.*, 1996), the data for monoisotopic REEs (Pr, Tb, Ho, and Tm) were not reported. This may be a disadvantage in identifying the tetrad effect in the REE pattern for the lanthanite-(Nd), and it may be better to be checked by using the ICP-MS data for lanthanite-(Nd) by Graham *et al.* (2007). In the case of the Hizen kimuraite-(Y) by Akagi *et al.* (1993), the analytical data for all REE but Y have been reported, and the W-type tetrad effect of the REE patterns of the kimuraite-(Y) was elucidated. However, one sample of kimuraite-(Y) from "middle layer" of a spherulitic aggregate (A) shows certainly a typical W-type tetrad effect, but another kimuraite sample from the "inner layer" of the same aggregate (A) exhibits a less symmetrical W-type tetrad effect. The REE patterns for the two samples of Hizen kimuraite-(Y) are similar, but not the same. According to Akagi *et al.* (1993), additional kimuraite sample taken from a separate spherulitic aggregate (B) shows a regular W-type tetrad effect similar to that from the "middle layer" of a spherulitic aggregate (A). We may ask a question

why the samples of Hizen kimuraite-(Y) from the same aggregate (A) appear to show fairly different tetrad effects even though they can be classified as the W-type.

The purpose of this paper is to examine the REE abundance data for lanthanite-(Nd) from Japan and New Zealand (Akagi *et al.*, 1993 and 1996; Graham *et al.*, 2007) and for kimuraite (Akagi *et al.*, 1993) in terms of Jørgensen-Kawabe equation for the lanthanide tetrad effect (Kawabe, 1992, 1999; Kawabe and Masuda, 2001; Kawabe *et al.*, 2008). The theoretical equation for the lanthanide tetrad effect has not been used in the previous REE studies of the lanthanite-(Nd) and kimuraite-(Y). Hence, this study may remove some ambiguities in the previous studies of the REE carbonate hydrates as mentioned above, and provide quantitative insights into the regularity of REE enrichments in the REE carbonate hydrate minerals.

### ANALYTICAL DATA FOR LANTHANITE AND KIMURAITHE

Table 1 cites the REE and Y analyses by ICP-MS for the lanthanite-(Nd) from the Whitianga quarry, Coromandel Peninsula, New Zealand (Graham *et al.*, 2007) and the REE data by ID-MS for the lanthanite-(Nd) from Hizen-cho, Higashi Matsuura-gun, Saga Prefecture, Kyushu, Japan (Akagi *et al.*, 1996). Table 2 also cites the REE data

**Table 1.** Reported REE data for lanthanite-(Nd), together with interpolated values for unreported REE and for correcting Ce anomalies.

(ppm)	Lanthanite-(Nd) Whitianga, New Zealand (Graham <i>et al.</i> , 2007)		Lanthanite-(Nd) Hizen, Japan (Akagi <i>et al.</i> , 1996)	
	Original data	Interpolated	Original data	Interpolated
La	$2.48 \times 10^5$		$1.51 \times 10^5$	
Ce	$1.49 \times 10^5$	$(5.76 \times 10^5)^*$	$1.01 \times 10^2$	$(2.89 \times 10^5)^*$
Pr	$6.36 \times 10^4$			$(3.55 \times 10^4)^*$
Nd	$2.74 \times 10^5$		$1.63 \times 10^5$	
Sm	$4.65 \times 10^4$		$3.05 \times 10^4$	
Eu	$1.21 \times 10^4$		$8.89 \times 10^3$	
Gd	$2.68 \times 10^4$		$2.85 \times 10^4$	
Tb	$2.29 \times 10^3$			$(2.29 \times 10^3)^*$
Dy	$8.19 \times 10^3$		$5.94 \times 10^3$	
Ho	$5.24 \times 10^2$			$(5.82 \times 10^2)^*$
Er	$6.12 \times 10^2$		$7.34 \times 10^2$	
Tm		$(4.83 \times 10)^*$		$(4.30 \times 10)^*$
Yb	$1.11 \times 10^2$		$0.919 \times 10^2$	
Lu	$1.11 \times 10$		$0.875 \times 10$	
Y	$1.72 \times 10^4$			

\* The interpolations were made in order to correct the Ce anomalies and to estimate the REE abundances unreported in the original studies in this study.

**Table 2.** Reported REE data for Kimuraite from Hizen, Japan

(ppm)	Kimuraite, Hizen, Japan (Akagi <i>et al.</i> , 1993)			Average of CI chondrites (Anders and Grevesse, 1989)
	Specimen A (middle layer)	Specimen A (inner layer)	Specimen B	
La	$4.94 \times 10^3$	$5.97 \times 10^3$ ( $9.15 \times 10^2$ )**	$5.70 \times 10^3$	0.2347
Ce	10 ( $1.35 \times 10^4$ )*	13.6 ( $3.39 \times 10^3$ )**	27 ( $1.52 \times 10^4$ )*	0.6032
Pr	$3.49 \times 10^3$	$2.69 \times 10^3$ ( $1.20 \times 10^3$ )**	$3.86 \times 10^3$	0.0891
Nd	$3.16 \times 10^4$	$1.96 \times 10^4$ ( $1.24 \times 10^4$ )**	$3.16 \times 10^4$	0.4524
Sm	$1.69 \times 10^4$	$7.86 \times 10^3$	$1.63 \times 10^4$	0.1471
Eu	$8.65 \times 10^3$	$3.88 \times 10^3$	$7.90 \times 10^3$	0.056
Gd	$5.17 \times 10^4$	$2.70 \times 10^4$	$4.59 \times 10^4$	0.1966
Tb	$7.48 \times 10^3$	$4.21 \times 10^3$	$7.13 \times 10^3$	0.0363
Dy	$4.07 \times 10^4$	$2.59 \times 10^4$	$4.28 \times 10^4$	0.2427
Ho	$7.63 \times 10^3$	$6.22 \times 10^3$	$8.80 \times 10^3$	0.0556
Er	$1.57 \times 10^4$	$1.51 \times 10^4$	$2.06 \times 10^4$	0.1589
Tm	$1.08 \times 10^3$	$1.44 \times 10^3$	$1.65 \times 10^3$	0.0242
Yb	$3.97 \times 10^3$	$4.88 \times 10^3$	$5.50 \times 10^3$	0.1625
Lu	$4.89 \times 10^2$	$6.14 \times 10^2$	$6.83 \times 10^2$	0.0243
Y	—	—	—	1.56

\* Estimates of Ce values (ppm) corrected for the negative Ce anomalies by interpolation in this study.

\*\* La, Ce, Pr and Nd values (ppm) corrected for the excesses in the “inner layer” kimuraite in this study.

for three kimuraite-(Y) samples from two different spherulitic aggregates A and B in Hizen-cho, Higashi Matsuura-gun, Saga Prefecture, Kyushu, Japan (Akagi *et al.*, 1993), in which monoisotopic REEs (Pr, Tb, Ho, and Tm) and polyisotopic REE have been determined by ID-MS and ICP-MS, respectively. In Table 2, the average REE abundances in the CI-chondrite (Anders and Grevesse, 1989) for normalization are also listed.

### JØRGENSEN-KAWABE EQUATION FOR LANTHANIDE TETRAD EFFECTS

We will regress the REE patterns for lanthanite-(Nd) and kimuraite-(Y) by Jørgensen-Kawabe equation for the lanthanide tetrad effect (Kawabe, 1992 and 1999; Kawabe and Masuda, 2001; Kawabe *et al.*, 2008):

$$\log(\text{REE})_n = A + (a+bq) q Z^* + (9/13) n(S) C_1 Z^* + m(L) C_3 Z^*, \quad (1)$$

where  $(\text{REE})_n$  stands for the REE abundance in the sample when normalized by

chondrite or a reference sample. The right-hand side of (1) is the improved equation of RSPET (Refined spin-pairing energy theory) for the tetrad effects in the thermochemical quantities of  $\Delta H_r^\circ$ ,  $\Delta S_r^\circ$  and  $\Delta G_r^\circ$  for ligand-exchange reactions for a pair of isomorphous REE(III) compound or complex (Kawabe, 1992 and 1999). This equation was successfully fitted to the  $\log K_d(\text{REE})$  data for solvent extractions by which Peppard *et al.* (1969) first proposed the lanthanide tetrad effect (Kawabe and Masuda, 2001), and it was also applied to the REE patterns for volcanic rocks with corrections for Eu anomalies and apparently irregular La and Ce abundances (Kawabe *et al.*, 2008). The parameters (A, a, b, C<sub>1</sub>, and C<sub>3</sub>) are the constants determined by the least-squares fitting of  $\log(\text{REE})_n$  data to eq. (1). The number of 4f electrons (q) corresponds to the ground-level electronic configuration of [Xe](4f)<sup>q</sup> for REE<sup>3+</sup>. Hence each REE<sup>3+</sup> is designated by q=Z-57, and the effective nuclear charge ( $Z^*=Z-32$ ) for 4f electrons of REE<sup>3+</sup> is also given by the number of 4f electrons of q, namely,  $Z^*=q+25$ . The constant coefficients of n(S) and m(L) are related to the total spin quantum number of S and the total orbital quantum number of L for the ground term (<sup>2S+1</sup>L) of [Xe](4f)<sup>q</sup>, and they are the negative coefficients or zero given theoretically for the respective ground-term energies of REE<sup>3+</sup> ions (Kawabe, 1992). The first and second terms in eq. (1) express a smooth variation across the REE series. The third and fourth terms represent the octad and intrinsic tetrad effect variations, which corresponds to the differences of Racah parameters (E<sup>1</sup> and E<sup>3</sup>) between the pair of REE(III) compound or complex series, when eq. (1) is applied to  $\log K_d(\text{REE})=-\Delta G_r/(2.303RT)$  at low temperatures. The sum of the third and fourth terms gives the overall tetrad effect.

The improved RSPET or Jørgensen-Kawabe equation (1) is based on the Slater-Condon-Racah theory of the atomic spectroscopy for free REE<sup>3+</sup> ions in vacuum as monatomic entities (Jørgensen, 1979). When the equation (1) is applied to  $\Delta H_r^\circ$ ,  $\Delta S_r^\circ$  and  $\Delta G_r^\circ$  for the ligand-exchange reactions of REE<sup>3+</sup> ions between a pair of REE(III) complexes or compounds, its application is limited to such a case that each REE(III) complex or compound series is an isomorphous one in which the coordination state of REE<sup>3+</sup> ion does not change across the series. In fact, however, fully isomorphous REE(III) complex series are scarcely found in real REE(III) compound or complexes, for example, REEO<sub>1.5</sub>(c), REEF<sub>3</sub>(c), and REE<sup>3+</sup>(aq) series are not isomorphous across the entire series. This gives an additional variation across the REE series that cannot be explained by the theoretical equation. The variations due to the structural changes of REE<sup>3+</sup> ions across the series are removed from the observed quantities before its application, in which available structural studies of the REE(III) compound or complex series of interest are considered carefully (Kawabe, 1992 and 1999).

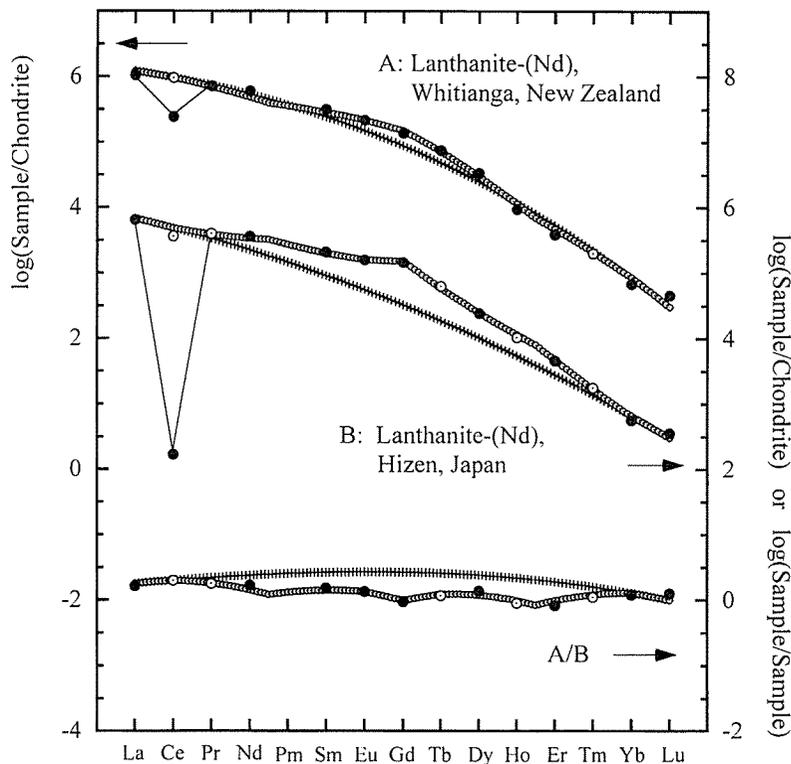
In this study, we will apply the equation (1) to REE patterns for lanthanite-(Nd) and kimuraite-(Y) relative to the chondrite or a reference sample, which do not immediately correspond to  $\log K_d(\text{REE})=-\Delta G_r/(2.303RT)$  for solvent extractions by Peppard *et al.* (1969). The  $\log K_d(\text{REE})$  values give the REE fractionation in a single step of equilibrium REE partitioning reaction, whereas the REE patterns represent the integral REE fractionation to produce the respective geochemical samples from the chondritic REE of the primitive Earth, or the difference in such integral REE fractionations between the sample and reference one (Kawabe *et al.*, 1998; Kawabe and Masuda, 2001; Kawabe *et al.*, 2008). Although the REE patterns for geochemical

samples are quite analogous to  $\log K_q(\text{REE})$ , they have different meanings when the pair of sample/reference does not correspond to a coexistent pair of materials in a geochemical system. Hence, there is no *a priori* reason to justify the application of the improved RSPET or Jørgensen-Kawabe equation (1) to  $\log(\text{REE})_n$ , but here is used eq. (1) only for a purpose to describe tetrad effects in REE patterns quantitatively. The importance of eq. (1) could be discussed *aposteriori* by referring to the resultant regressions and other geochemical data relevant to the genesis of the geochemical samples.

## RESULTS

### 1. EE patterns for lanthanite-(Nd)

The chondrite-normalized REE patterns for the lanthanite-(Nd) from Whitianga, New Zealand, and from Hizen, Kyushu, Japan, can be regressed successfully by the Jørgensen-Kawabe equation for the tetrad effect, and the results are shown in Fig. 1.



**Fig. 1** The chondrite-normalized REE patterns for Whitianga lanthanite-(Nd) (Graham, 2007) and Hizen lanthanite-(Nd) (Akagi *et al.*, 1996) regressed by the Jørgensen-Kawabe equation (1). Filled circles show REE data reported by the original authors, and open circles are the interpolated values in this paper. The REE enrichment pattern for Whitianga lanthanite-(Nd) relative to Hizen lanthanite-(Nd) in the logarithmic scale (lowest panel) is also regressed by the Jørgensen-Kawabe equation (1).

Both the lanthanites exhibit negative Ce anomalies, so that they were corrected by interpolation. In the least-squares fitting of REE data for the lanthanite-(Nd) from Whitianga, New Zealand, the interpolated values for Ce and Tm (open circles in Fig. 1) were combined with the other reported REE analyses, and used as a set of REE data for the regression. The interpolated values are listed in Table 1.

In the case of the lanthanite-(Nd) from Hizen, Kyushu, Japan, the reported Ce analysis was replaced by the interpolated one, and such interpolation values were used for the unreported monoisotopic REEs (Pr, Tb, Ho, and Tm) as the input data. Table 1 lists the interpolated values. The least-square fittings of chondrite-normalized REE patterns for the lanthanite-(Nd) from Whitianga and from Hizen are fairly satisfactory (Fig. 1). It is worthy to note that spurious results of fitting are obtained if the interpolated values are not joined with the reported REE data for the Hizen lanthanite.

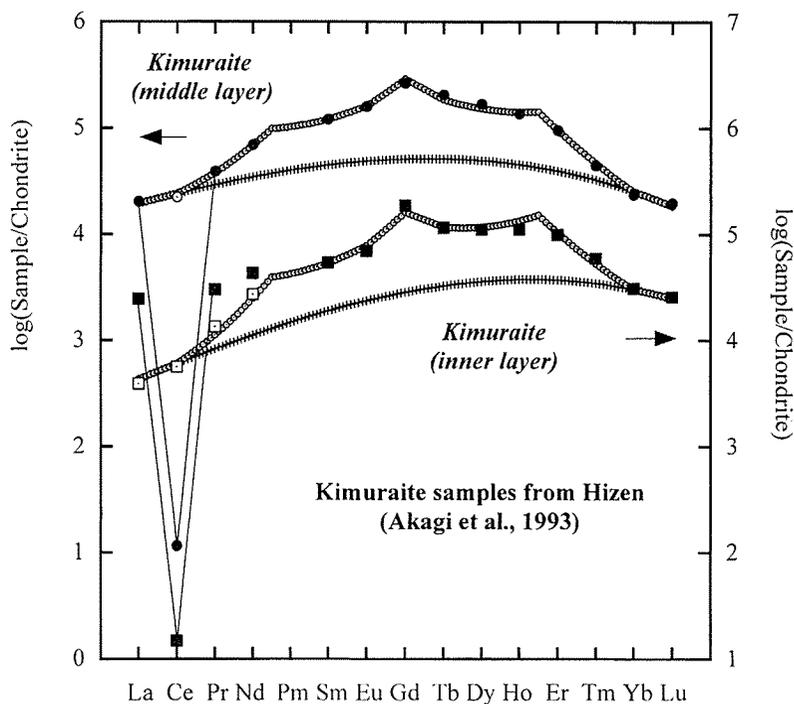
The light REE enrichment trends expressed by the smooth terms of (1) are fairly similar between the two lanthanites. The differences in  $\log(\text{REE}/\text{chondrite})$  values between the lanthanite samples from Whitianga and Hizen were also regressed by the equation (1) as shown in the lower panel of Fig. 1. The differences exhibit a small convex tetrad effect compatible with the Jørgensen-Kawabe equation (1). The strong trends of light REE enrichment in lanthanites are cancelled almost totally between the two lanthanite samples, and then the small convex tetrad effect emerges as a result of the mutual normalization.

## 2. REE patterns for kimuraite-(Y)

Akagi *et al.* (1993) demonstrated that two kimuraite-(Y) samples from the middle and inner layers of a spherulitic aggregate (A) and one kimuraite-(Y) sample from a separate spherulitic aggregate (B) in the Cenozoic alkali-olivine basalt in Hizen, Kyushu, Japan, indicate W-type tetrad effects characterized by concave tetrad curves, together with the extremely negative Ce anomalies. It has been clearly shown in the original report that the two kimuraite samples from the middle layer of a spherulitic aggregate (A) and from another aggregate (B) exhibit almost the same regular W-type tetrad effect. We also confirmed this in our regression by the equation (1). However, the kimuraite sample from the inner layer of a spherulitic aggregate (A) shows a different W-type tetrad effect. This is shown in Figs. 2 and 3, together with the kimuraite sample from the middle layer of the same aggregate. We will focus the somewhat contrasting REE features between the “middle layer” and “inner layer” kimuraite samples in the same spherulitic aggregate (A).

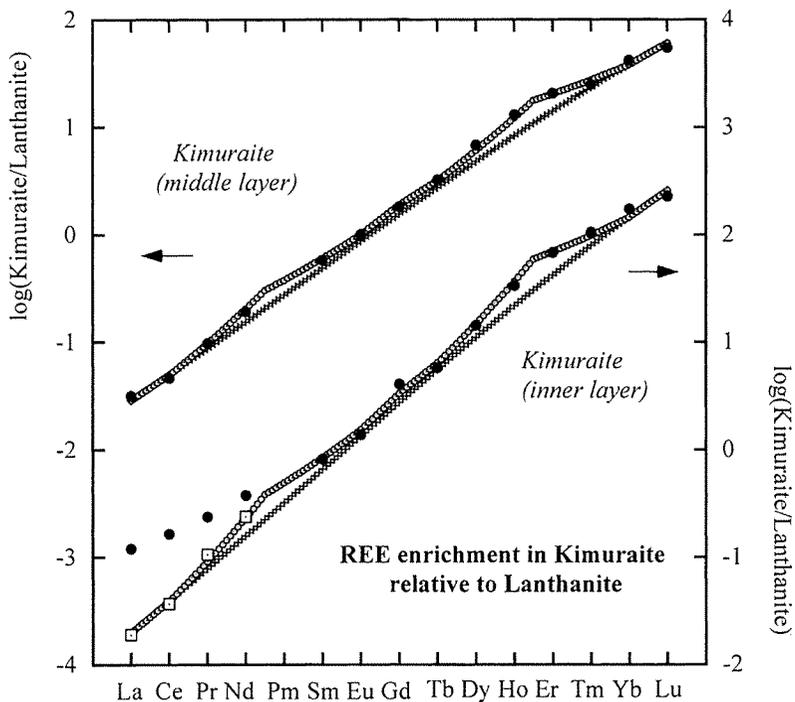
As shown in Fig. 2, the “middle layer” kimuraite-(Y) displays a chondrite-normalized REE pattern that can be regressed by the Jørgensen-Kawabe equation (1) almost immediately only when corrected for the Ce anomaly. Nevertheless, the “inner layer” kimuraite-(Y) does not match the theoretical equation only if its Ce anomaly is corrected (Fig. 2). If the less symmetrical tetrad effect is regressed by the equation (1), the corrections for La, Ce, Pr, and Nd shown as the open squares in Fig. 2 are necessary. Such corrections for the four light REEs have been estimated from the regular REE enrichment pattern for the “middle layer” kimuraite relative to lanthanite (Fig. 3).

Figure. 3 illustrates that the REE abundances of the “middle layer” kimuraite relative to the Hizen lanthanite shown in Fig. 1, are immediately fitted to the Jørgensen-Kawabe



**Fig. 2** The chondrite-normalized REE patterns for two Hizen kimuraite-(Y) samples of “middle layer” and “inner layer” of a spherulitic aggregate (A) reported by Akagi et al. (1993) regressed by the Jørgensen-Kawabe equation (1). Filled circles or squares show REE data by the original authors. An open square for Ce of the “middle layer” kimuraite indicates the Ce value corrected for the negative Ce anomalies. Four open squares of the “inner layer” kimuraite show the values corrected for the excesses of La, Pr, and Nd and for the Ce anomaly.

equation (1), though their Ce anomalies are corrected. The absence of octad effect means that their octad effects in their chondrite-normalized REE patterns are the same between the “middle layer” kimuraite and the lanthanite (Figs. 1 and 2). There is recognized, however, a small concave tetrad effect corresponding to a difference in the fourth term of (1). In contrast to the “middle layer” kimuraite, the abundances of La, Ce, Pr, and Nd of the “inner layer” kimuraite appear to be corrected to the data points given by open squares in Fig. 3 in order to make the other REE data compatible with the theoretical equation. Referring to the regular pattern of the “middle layer” kimuraite in Fig. 3, we have repeated the least-squares fitting of data sets of the “inner layer” kimuraite with corrections for light REEs, and then we have estimated the excesses of La, Ce, Pr, and Nd in the “inner layer” kimuraite. Table 2 lists the La, Ce, Pr, and Nd values corrected their excesses. Although the excess of Ce is for the hypothetical Ce abundance without its anomaly, those for La, Pr, and Nd possibly may be real excesses (Fig. 3). The REE enrichments in the “inner layer” kimuraite relative to the “middle layer” kimuraite are shown in Fig. 4, where the open circles show the light REE values corrected for their excesses in the “inner layer”



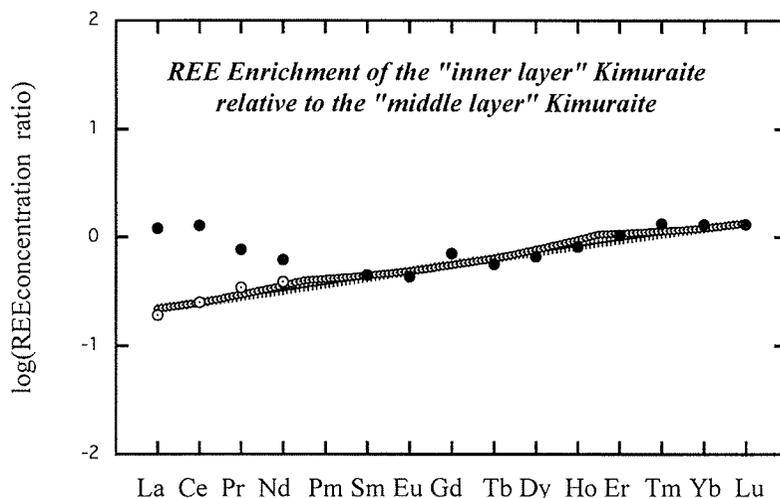
**Fig. 3** The REE enrichment pattern for the “middle layer” kimuraite relative to lanthanite, can be regressed by the Jørgensen-Kawabe equation (1) immediately, but this is not true for the “inner layer” kimuraite. Filled circles are the ratios calculated from the original REE data for the kimuraite samples reported by Akagi *et al.* (1993) and those for the Hizen lanthanite-(Nd) listed in Table 1, except for the points for Ce. The filled circles for Ce are calculated from the interpolated Ce values in Tables 1 and 2. Open squares for the light REE of the “inner layer” kimuraite are the values corrected for the excesses of La, Ce, Pr, and Nd. They make the REE pattern for the “inner layer” kimuraite compatible with the theoretical equation (1).

kimuraite. The less symmetrical W-type tetrad effect of the “inner layer” kimuraite becomes comparable with the symmetrical one of the “middle layer” kimuraite by the corrections of excesses of light REE (Figs. 2 and 4).

## DISCUSSION

### 1. REE abundances in lanthanite compatible with Jørgensen-Kawabe equation

We have confirmed that Jørgensen-Kawabe equation (1) for the tetrad effect quantitatively describes the chondrite-normalized REE patterns for the lanthanite-(Nd) from the Whitianga quarry, New Zealand (Graham *et al.*, 2007) and Hizen-cho, Higashi Mastuura-gun, Saga Prefecture, Japan (Akagi *et al.*, 1996), except for their negative Ce anomalies. Their strong trends of light REE enrichments are fairly similar between the two samples, whereas the Hizen lanthanite exhibits a slightly greater W-type tetrad effect than the Whitianga one. This difference is clearly seen as a regular convex tetrad effect in the REE pattern of the Whitianga lanthanite normalized by the Hizen



**Fig. 4** The REE pattern for the “inner layer” kimuraite relative to the “middle layer” kimuraite, when corrected for the excessive light REE of the “inner layer” kimuraite as in Fig. 3, becomes compatible with the Jørgensen-Kawabe equation (1). Filled circles are the ratios calculated from the original REE data by Akagi *et al.* (1993), except Ce. The filled circle for Ce is the interpolation value as in Fig. 3. The open circles for light REE of the “inner layer” kimuraite correspond to the open squares of Fig. 3.

lanthanite (Fig. 1).

Since both lanthanite samples were possibly precipitated from local hydrothermal solutions enriched in REEs, the regular convex tetrad effect may correspond to the difference in REE solution chemistry between the two local geochemical solutions. However, such solution REE themselves could be derived from local crustal rocks during interactions between solutions and crustal rocks. Therefore, the regular convex tetrad effect reflects mostly the difference in REE characteristics between the local crustal rocks occupying Whitianga and Hizen areas, respectively. One of the present authors (Kawabe, 1996) reported a similar convex tetrad effect in the REE pattern for “Post-Archean Australian shale (PAAS)” normalized by “North American shale composite (NASC)”. This is an example that the difference in REE abundances of average crustal rocks is approximately expressed by a small regular tetrad effect with convexity or concavity. The present result of a convex tetrad effect (Fig. 1) also may be an analogous example.

The pair of the “middle layer” kimuraite and lanthanite from Hizen could be a coexistent REE mineral pair, so that the observed steep trend with a small intrinsic tetrad effect (Fig. 3) may represent the characteristics REE fractionation between the coexisting REE mineral pair of kimuraite and lanthanite. This provides a key to understanding the reason why the kimuraite from “inner layer” does not exhibit a typical W-type tetrad effect unlike the “middle” kimuraite (Fig. 2).

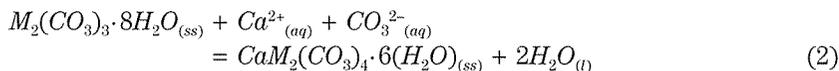
## 2. Excesses of light REEs in the “inner layer” kimuraite

We have found that the “inner layer” kimuraite involves some excesses of light REEs

in view of the regular REE fractionation trend for the “middle” kimuraite/lanthanite pair (Fig. 3). The correction of such excesses in La, Ce, Pr and Nd makes the REE patterns for the “inner layer” kimuraite regular, and all of them become compatible with the Jørgensen-Kawabe equation (1) (Figs. 2, 3, and 4). Recently, we have reported such a Hizen kimuraite sample similar to the “inner layer” kimuraite by Akagi *et al.* (1993): Slender patches with micron~submicron widths distribute inside of kimuraite grains, and the inclusions may be the lanthanite-like material in chemical composition (Jiao *et al.*, 2011 and in preparation). Therefore, our corrections for excess La, Ce, Pr, and Nd in the “inner layer” kimuraite (Figs. 2, 3, and 4) may be reasonable and acceptable, when the “inner layer” kimuraite by Akagi *et al.* (1993) is analogous to the kimuraite having impurity of lanthanite-like material reported by Jiao *et al.* (2011).

### 3. Tetrad effect of REE fractionation for the kimuraite/lanthanite pair

We will add discussion on the possible impact of the present results on REE geochemistry. The regular steep trend with a small intrinsic tetrad effect (Fig. 3) is possibly the equilibrium REE fractionation between the coexistent mineral pair of kimuraite and lanthanite. This may be comparable with  $\log K_4(\text{REE})$  values for the solvent extraction systems by Peppard *et al.* (1969), which are the experimental evidence for their proposal of the lanthanide tetrad effect and compatible with the improved RSPET or Jørgensen-Kawabe equation (Kawabe and Masuda, 2001). The formation of kimuraite from lanthanite in a reaction with solution may be written as below,



where  $M$  denotes each trivalent REE including Y. The equilibrium constant  $K$  for (2) is given in terms of the activities of relevant species,

$$K(M) = \frac{a(\text{Ca}M_2(\text{CO}_3)_4 \cdot 6(\text{H}_2\text{O}))}{a(M_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O})} \cdot \frac{a^2(\text{H}_2\text{O})}{a(\text{Ca}^{2+}) \cdot a(\text{CO}_3^{2-})}, \quad (3)$$

and it follows that

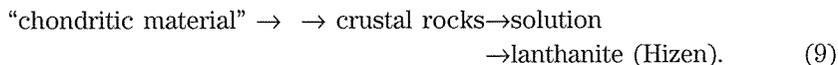
$$\log K(M) = -\Delta G_f^0(M)/(2.303RT), \quad (4)$$

where  $\Delta G_f^0(M)$  is the Gibbs free energy change for the reaction (2) at the given T and P conditions. The activity ratio of  $M$ -kimuraite to  $M$ -lanthanite in (3) is written by using the activity coefficient ( $\lambda_i$ ) and molar fraction ( $X_i$ ) for each  $M$ -component of kimuraite or lanthanite:

$$\frac{a(\text{Ca}M_2(\text{CO}_3)_4 \cdot 6(\text{H}_2\text{O}))}{a(M_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O})} = \frac{\lambda_{kim}(M) \cdot X_{kim}(M)}{\lambda_{lan}(M) \cdot X_{lan}(M)} = \frac{\lambda_{kim}(M)}{\lambda_{lan}(M)} \cdot \alpha \cdot \frac{[M]_{kim}}{[M]_{lan}}, \quad (5)$$

where the second equation means that the molar fraction ratio can be converted into the ratio of weight concentrations of  $M$  between kimuraite and lanthanite expressed as  $[M]_{kim}/[M]_{lan}$ . The constant  $\alpha$  is a factor for the conversion of the molar fraction ratio into the weight concentration one. Hence,  $K(M)$  of (3) is written as





If the REE fractionation between local thermal solution and lanthanite is roughly the same at the two locations of New Zealand and Kyushu Japan at their formation times, the apparent REE fractionation of the convex tetrad effect between the two lanthanites (Fig. 1) is attributable to the differences in the REE abundances of the average crustal rocks in the two areas. When we trace back to the past along the chain of geochemical reactions for any geochemical sample, it may link with the “chondritic material” of the primitive Earth. We would like to consider the chondrite-normalized REE patterns for geochemical samples in view of the reaction chains like (8) and (9).

We will divide the integral REE fractionations in the reaction chains of (8) and (9) into two steps: the first step is from the “chondritic material” to crustal rocks, and the second one is from crustal rocks to lanthanites. And then we assume that REE fractionation in each step can be approximately expressed by the Jørgensen-Kawabe equation. All the parameters of the equation ( $A$ ,  $a$ ,  $b$ ,  $C_1$ , and  $C_3$ ) are constant and additive, so that the chondrite-normalized REE pattern for each lanthanite as the sum of the two steps can also be expressed by a single Jørgensen-Kawabe equation like the results of Fig. 1. Even if we divide the integral process into more than two steps, our conclusion is unchanged. The essential points are that REE fractionation in each step is approximately described by Jørgensen-Kawabe equation, and that each parameter of the equation ( $A$ ,  $a$ ,  $b$ ,  $C_1$ , or  $C_3$ ) is approximately additive in successive chains of the REE fractionation. In particular, the constant parameters of  $C_1$  and  $C_3$  determining the overall tetrad effect are summed up over the successive chains of the REE fractionation between geochemical materials. This might be an interpretation of the tetrad effects observed in the chondrite-normalized REE pattern for geochemical samples in view of Jørgensen-Kawabe equation.

## CONCLUSIONS

We have examined the REE abundance patterns for lanthanite-(Nd) and kimuraite-(Y) by using the Jørgensen-Kawabe equation for the lanthanide tetrad effect. The chondrite-normalized REE pattern for lanthanite-(Nd) samples from the Whitianga quarry, New Zealand (Graham *et al.*, 2007) and Hizen, Higashi Mastuura, Japan (Akagi *et al.*, 1996), can be regressed successfully by the theoretical equation, except for their Ce anomalies. When the Whitianga lanthanite-(Nd) is normalized by the Hizen lanthanite, their strong trends of light REE enrichment are cancelled mutually, and there remains a small convex tetrad effect.

Two kimuraite-(Y) specimens coexistent with the Hizen lanthanite-(Nd) show similar W-type tetrad effects (Akagi *et al.*, 1993). However, one Hizen kimuraite indicates a typical symmetrical tetrad effect of the W-type, whereas the other does a less symmetrical one. The chondrite-normalized REE pattern for the kimuraite-(Y) specimen with a typical W-type tetrad effect is immediately fitted to the theoretical equation, but the other kimuraite with a less symmetrical tetrad effect cannot be regressed by the equation unless the data for light REEs are corrected. We suggest that the Hizen

kimuraite indicating a less symmetrical tetrad effect involves some excesses of light REE, like the kimuraite sample reported by us (Jiao *et al.*, 2011). Such excesses have been determined by using a regular REE fractionation for the kimuraite/lanthanite pair and the theoretical equation.

The REE patterns for lanthanite-(Nd) and kimuraite-(Y) with the tetrad effects are certainly compatible with Jørgensen-Kawabe equation of the refined spin-pairing energy theory (RSPET) for  $[Xe]4f^n$  configurations. The theoretical equation is important even in considering the regularity of REE distributions in the representative REE minerals of lanthanite-(Nd) and kimuraite-(Y).

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## REFERENCES

- Akagi, T., Nakai, S., Shimizu, H., Masuda, A., 1996. Constraint on the geochemical stage causing tetrad effect in kimuraite: Comparative studies on kimuraite and its related rocks from REE pattern and Nd isotope ratio. *Geochem. J.*, **30**, 139-148.
- Akagi, T., Shabani, M. B., Masuda, A., 1993. Lanthanide tetrad effect in kimuraite  $[CaY_2(CO_3)_4 \cdot 6H_2O]$ : Implication for a new geochemical index. *Geochim. Cosmochim. Acta*, **57**, 2899-2905.
- Dal Negro, A., Rossi, G., and Tazzoil, V. (1977) The crystal structure of lanthanite. *Am. Mineral.*, **62**, 142-146.
- Anders, E., Grevesse, N., 1989. Abundances of the elements: Meteoritic and solar. *Geochim. Cosmochim. Acta*, **53**, 197-214.
- Graham, I. T., Pogson, R. E., Colchester, D. M., Hergt, J., Martin, R., William, P. A., 2007. Pink lanthanite-(Nd) from Whitianga quarry. Coromandel Peninsula, New Zealand. *Canadian Mineral.*, **45**, 1389-1396.
- Jiao, W. F., Kawabe, I., Kato, T., 2011. Reexamination of natural kimuraite and synthetic experiment of kimuraite. *Abst. 58th Meet. Geochem. Soc. Japan, Sapporo, Japan*, p. 404.
- Jørgensen, C. K., 1979. Theoretical chemistry of rare earths. In: *Handbook on the Physics and Chemistry of Rare Earths* (Gschneider, K. A. Jr. and L. Eyring, Eds.), 3, 111-169, North-Holland, Amsterdam.
- Kawabe, I., 1992. Lanthanide tetrad effect in the  $Ln^{3+}$  ionic radii and refined spin-pairing energy theory. *Geochem. J.*, **26**, 309-335.
- Kawabe, I., 1996. Convex tetrad effect variations in REE abundances of "North American shale composite" and "Post-Archean Australian shale". *Geochem. J.*, **30**, 149-153.
- Kawabe, I., 1999. Thermochemical parameters for solution of lanthanide(III) ethylsulphate and trichloride hydrate series: Evidence for tetrad effect and hydration change in aqua  $Ln^{3+}$  ion series. *Geochem. J.*, **33**, 249-265.
- Kawabe, I., Masuda, A., 2001. The original examples of lanthanide tetrad effect in solvent extraction: A new interpretation compatible with recent progress in REE geochemistry. *Geochem. J.*, **35**, 215-224.
- Kawabe, I., Tanaka, K., Takahashi, T., Minagawa, T., 2008. Evidence for lanthanide tetrad effect in mafic volcanic rocks; Concave tetrad effects in REE patterns for MORB and alkali olivine basalt in western Kyushu, Japan. *J. Earth Planet. Sci. Nagoya Univ.*, **55**, 1-21.
- Kawabe, I., Toriumi, T., Ohta, A., Miura, N., 1998. Monoisotopic REE abundances in seawater and the origin of seawater tetrad effect. *Geochem. J.*, **32**, 213-229.
- McLennan, S. M., 1994. Rare earth element geochemistry and the "tetrad" effect. *Geochim.*

*Cosmochim. Acta*, **58**, 2025-2033.

- Miyawaki, R., Kuriyama, J., and Nakai, I. (1993) The redefinition of tenerite-(Y),  $Y_2(CO_3)_3 \cdot 2-3H_2O$ , and its crystal structure. *Am. Mineral.*, **78**, 425-432.
- Miyawaki, R., Nakai, I., 1996. Crystal chemical aspects of rare earth minerals. In: *Rare Earth Minerals* (Jones, A. P., Wall, F., Williams, C. T. Eds.) Chapman & Hall. London, 21-40.
- Nagashima, K., Miyawaki, R., Takase, J., Nakai, I., Sakurai, K., Matsubara, S., Kato, A. Iwano, S., 1986. Kimuraite,  $CaY_2(CO_3)_4 \cdot 6H_2O$ , a new mineral from fissures in an alkali olivine basalt from Saga Prefecture, Japan, and new data on lokkaite. *Am. Mineral.*, **71**, 1028-1033.
- Peppard, D. F., Mason, G. W., Lewey, S., 1969. A tetrad effect in the liquid-liquid extraction ordering of lanthanides (III). *J. inorg. nucl. Chem.*, **31**, 2271-2272.